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# PIKOLIN KISLOTANING TOLUIDIN IZOMERLARI BILAN REAKSIYASIDAN SINTEZ QILINGAN AMID XOSILALARINING TUZILISHINI ZAMONAVIY FIZIK-KIMYOVIY TADQIQOT USULLARI YORDAMIDA TASDIQLASH

Annotatsiya

Pikolin kislotani toluidin izomerlari bilan reaksiyasidan olingan amid xosilalarining individualligi va ularning tuzilishi yupqa qatlam xromatografiyasi (YuQX) va IQ, YaMR, MACC spektroskopiya usullari bilan tasdiqlandi.

**Kalit so’zlar:** pikolin kislota, toluidin, amid, IQ spektr, $^{1}$H YaMR spektr, $^{13}$C YaMR spektr, MASS spektr.

# ПОДТВЕРЖДЕНИЕ СТРУКТУРЫ ПРОИЗВОДНЫХ АМИДОВ, СИНТЕЗИРОВАННЫХ РЕАКЦИЕЙ ПИКОЛИНОВОЙ КИСЛОТЫ С ТОЛУИДИНОВЫМИ ИЗОМЕРАМИ СОВРЕМЕННЫМИ МЕТОДАМИ ФИЗИКО-ХИМИЧЕСКИХ ИССЛЕДОВАНИЙ

Аннотация

Индивидуальность свойств амидов, полученных в результате реакции пиколи-новой кислоты с изомерами толуидина, и их структуры подтверждена методами тонкослойной хроматографии (ТСХ) и ИК, ПМР, МАСС-спектроскопии.

**Ключевые слова:** пиколиновая кислота, толуидин, амид, ИК-спектр, спектр $^{1}$H ПМР, спектр $^{13}$C ПМР, МАСС-спектр.

# CONFIRMATION OF THE STRUCTURE OF AMIDE DERIVATIVES SYNTHESIZED BY THE REACTION OF PICOLIC ACID WITH TOLUIDINE ISOMERS USING MODERN METHODS OF PHYSICAL AND CHEMICAL RESEARCH

Annotation

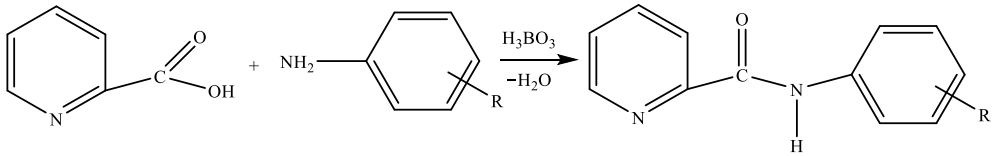
The individual properties of amides obtained from the reaction of picolinic acid with toluidine isomers and their structure were confirmed by thin-layer chromatography (TLC) and IR, NMR, MASS spectroscopy.

**Key words:** picolinic acid, toluidine, amide, IR spectrum, $^{1}$H NMR spectrum, $^{13}$C NMR spectrum, MASS spectrum.

**Kirish.** Ma'lumki, karbon kislotalar, aminlar va ularning hosilalari organik birikmalar orasida keng tarqalgan, nazariy va amaliy ahamiyati yuqori bo'lgan birikmalar hisoblanadi. Shu jumladan piridinkarbon kislotalarning hosilalaridan ham analitik kimyoda organik reagent, kompleks birikmalar olishda ligandlar sifatida, yangi kimyoviy birikmalar sintez qilishda foydalanib kelinmoqda. Shuningdek, piridinkarbon kislotalarning hosilalari orasida ko'plab yuqori biologik faol birikmalar aniqlangan bo'lib tibbiyot va farmasevtika sohalarining rivojlanishida alohida ahamiyat kasb etadi [1]. Kompleks birikmalar kimyosida ayniqsa 2-piridinkarbon kislotasining ligandlik hossasi tegishlicha o'rganilgan bo'lib, karboksil guruhidagi -vodorod va piridin halqasidagi azot atomining taqsimlanmagan juft elektronlari hisobiga turli oraliq metallar bilan kompleks birikmalar hosil qilishi aniqlangan [2]. Piridinkarbon kislotalari singari ularning amidlarida ham ligandlik hususiyati saqlanib qoladi [3]. 2-Piridinkarbon kislotasi amidlari molekulasining piridin frag-mentidagi azot atomining taqsimlanmagan juft elektronlari va elektronga boy karbo-nil guruhi kislorod atomi hisobiga turli metallar bilan koordinatsion bog’lanish hosil qilish imkoniyatiga ega bo'ladi:

Karbon kislotalarning aromatik aminlar bilan reaksiyalaridan bir malekula suv ajralishi natijasida kislotalarning almashingan arilamidlari hosil bo'ladi [4-5].

**Tajriba natijalari va tahlili.** Pikolin kislotani toluidin izomerlari bilan reak-siyalari natijasida ham bir molekula suvning chiqib ketishi bilan pikolin kislotaning tolil amidlari hosil bo’ladi. Reaksiya quyidagi tenglama bo’yicha boradi.




R = o-$CH_3$, m-$CH_3$, p-$CH_3$

Sintez qilingan amid hosilalarining individualligi va ularning tuzilishi yupqa qatlam xromatografiyasi (YuQX), IQ, YaMR, MACC spektroskopiya usullari bilan tasdiqlandi.

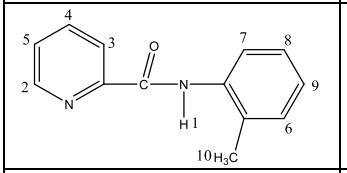
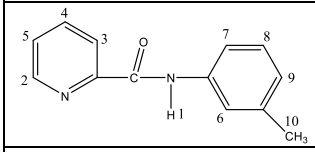
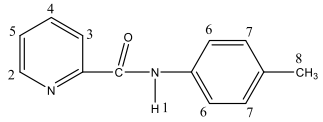
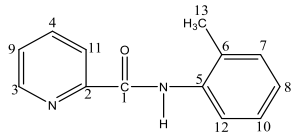
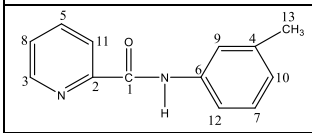
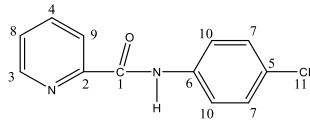
Pikolin kislota, toluidin izomerlari va ularni amidlash reaksiyalari natijasida olingan amid mahsulotlarning IQ spektrlari taqqoslanganda quyidagi natijalar kuzatil-di. Pikolin kislotaning IQ spektridagi xarakterli tebranishlar ν=1720 $sm^{-1}$ da karbonil guruhi (C=O); ν=3401 $sm^{-1}$ da karboksil guruhidagi vodorod bog’lanishli OH ga xos valent tebranishlar [6], toluidin izomerlarining IQ spektrida xarakterli tebranishlar o-toluidinda ν=3480-3396 $sm^{-1}$ valent, δ=1621 $sm^{-1}$ va δ=6845 $sm^{-1}$ larda $NH_2$ ga xos diformatsion [7], p-toluidinda ν=3470-3388 $sm^{-1}$ valent, δ=1698 $sm^{-1}$ va δ=651 $sm^{-1}$ larda $NH_2$ ga [8] xos diformatsion tebranishlar kuzatiladi. Bu birikmalarning o’zaro tasirlashishi natijasida hosil bo’lgan N-(2-metilfenil)-pikolinamid va N-(4-metilfenil)-pikolinamidlarining IQ spektrida esa pikolin kislotadagi OH ga va aminlardagi $NH_2$ ga tegishli yutilish chastotalari yo’qolib amid bog’idagi N–H guruhiga xos bo’lgan ν = 3350 $sm^{-1}$, 3340 $sm^{-1}$ da valent va δ = 1545 $sm^{-1}$, 1520 $sm^{-1}$ da diformatsion, ν = 1695 $sm^{-1}$, 1675 $sm^{-1}$ da sohada C=O guruhining tebranishlariga xos chastotalarning mavjudligi kislota amidlari hosil bo’lganligini tasdiqlaydi.

Reaksiya mahsulotlarining YaMR spektrlaridagi proton va uglerod atomla-rining kimyoviy siljishi 1-jadvalda keltirilgan.

*1-jadval*

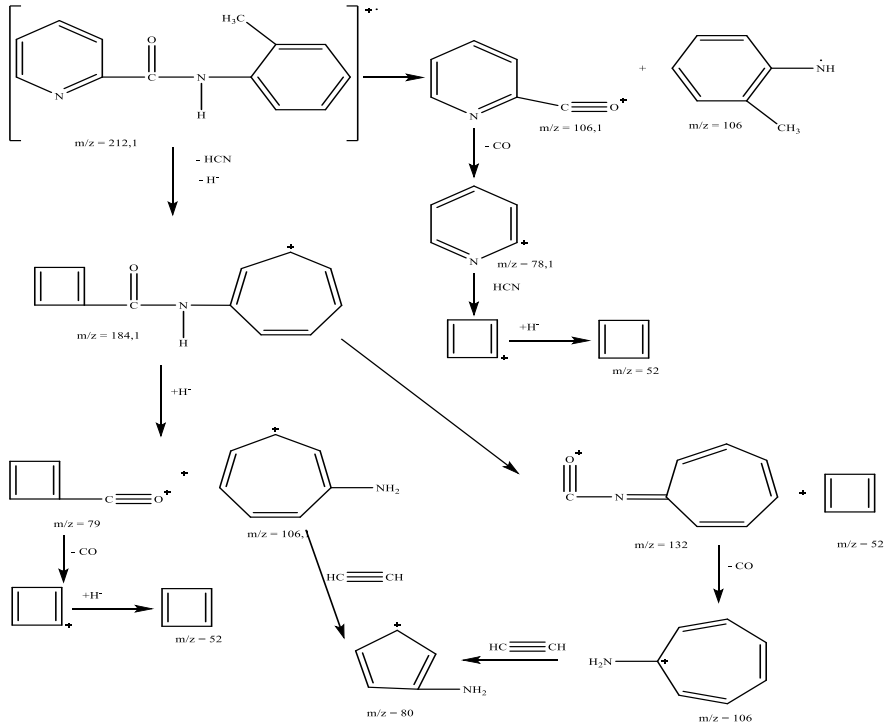
$^{1}H$ va $^{13}C$ YaMR spektrlarida proton va uglerodlarning kimyoviy siljishi

Reaksiya mahsulotlarining $^{1}H$ YaMR spektrlarida pikolin kislotadagi gidroksil guruhi (-OH) vadorod atomiga tegishli va

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 10,10 | 8,63 | 8,32 | 8,29 | 7,91 | 7,48 | 7,28 | 7,23 | 7,09 | 2,43 | | | |
|  | 10,0 | 8,6 | 8,3 | 7,89 | 7,59 | 7,46 | 7,28 | 7,28 | 7,04 | 2,39 | | | |
|  | 9,97 | 8,6 | 8,29 | 7,9 | 7,67 | 7,46 | 7,19 | 2,34 | | | | | |
|  | 162 | 150,26 | 148,21 | 137,77 | 136,04 | 130,53 | 128,12 | 127,01 | 126,52 | 124,66 | 122,50 | 121,41 | 17,86 |
|  | 162,03 | 149,96 | 148,03 | 139,05 | 137,74 | 128,98 | 126,48 | 125,22 | 122,44 | 120,4 | 116,87 | 112,31 | 21,61 |
|  | 161,97 | 151,05 | 148,05 | 137,76 | 135,35 | 134,03 | 129,7 | 126,48 | 122,46 | 119,69 | 21,04 | | |

toluidinlardagi amino guruhi (-$NH_2$) vodorod atomlariga tegishli signallar yo’q bo’lib, 9,97-10,10 m.u. larda amid guruhi (-NH-) guruhi protonlarining singlet signallari, shuningdek 7,04-8,32 m.u. larda aromatik xalqaning turli holatlaridagi protonlarining singlet, dublet, triplet signallari, 2.34-2.43 m.u. larda $CH_3$ guruhi protonlarining singlet signallari kuzatildi. $^{13}C$ YaMR spektrlarida ham pikolin kislotadagi -CO guruh uglerod atomlariga tegishli kimyoviy siljishlar o’rniga 162,03-161,97 ppm da amid bog’idagi karbonil (-CO-) guruhi ugle-rodlariga tegishli kimyoviy siljishlar kuzatildi. Spektr natijalarining tahlili pikolin kislotasining toluidinlar bilan olib borilgan reaksiyalaridan amid bog’i tutuvchi mah-sulotlar hosil bo’lganligini ko’rsatadi.

MASS spektr tahliliga ko’ra pikolin kislota va toluidin izomerlaridan olingan amid xosilalarining elektronlar oqimi bilan tasirlashishidan barchasida massasi m/z=212,1 ga teng bo’lgan molekulyar ionlar hosil bo’ldi. Malekulyar ionlardan dissotsialanish jarayoni natijasida turli massali bo’lakli ion hosil bo’ldi. Quyida N-(2-metilfenil)-pikolinamidning elektronlar oqimi bilan tasirlashishidan hosil bo’lgan molekulyar va bo’lakli ionlari keltirilgan.

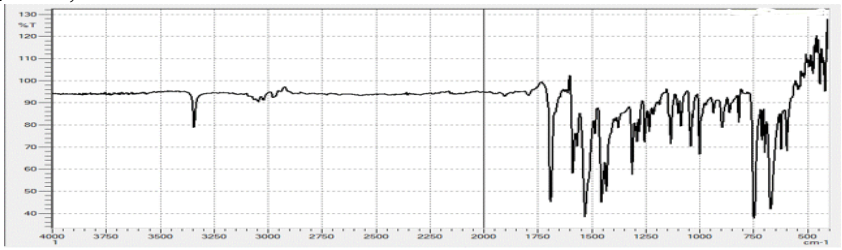



**Tajribalar qismi.** Sintez qilib olingan amidlarning individualligi yupqa qat-lamli xromatografiya (YuQX) usulida «Sorbfil» (Россия), «Whatman® UV-254» UV lampasida, Aluminum TLC plate F-254 (MFR: Qingdao Seeking Technology Co.,Ltd) plastinkalarida tekshirildi, elyuentlar sifatida esa benzol:atseton=5:1 nisbat-da ishlatildi. Sitez qilingan birikmalarning IQ-spektrlari Shimadzu firmasining IRAFFINITY-1S IR-Fourier spektrometrida KBr li tabletkalarda, $^{1}$H va $^{13}$C NMR spektrlari JNM-ECZ400R spektrometrida (JEOL, Yaponiya) CCl3D eritmalarida $^{1}$H uchun 400 MGts ish chastotasida qayd etilgan. TMS (0 ppm) $^{1}$H NMR spektrlarida ichki standart sifatida ishlatilgan. $^{13}$C NMR spektrlarida erituvchining kimyoviy silji-shi ($CCl_3D$, TMSga nisbatan 49,00 ppm) ichki standart sifatida ishlatilgan. Birikma-larning suyuqlanish harorati BMP-1C modelida 220V/50Hz da (Xitoy) asbobida o’lchandi

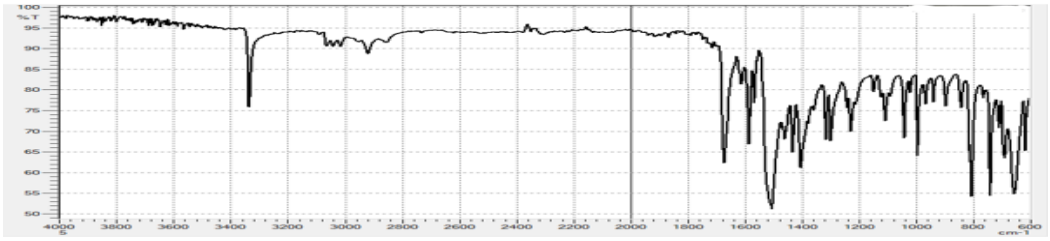
***N-(2-metilfenil)-pikolinamid***: 0,615 gr (0,005 mol) pikoli kislota va 1,07 gr (0,01 mol) o-toluidindan 0,062 gr (0,005 mol) $H_3BO_3$ katalizator ishtirokida sintez qilindi. $R_f$=0,837, suyqlanish harorati $T_s$=62ºC. IQ spektr (KBr $sm^{-1}$) ν=3350 (-NH), δ=1545 (-NH), ν=1695 (-CO-). $^{1}$H NMR (600 MHz, $CCl_3D$) δ 10.10 (s, 1H), 8.63 (d, *J* = 4.8 Hz, 1H), 8.32 – 8.29 (m, 2H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 7.6, 4.7 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (151 MHz, $CCl_3D$) δ 162.00, 150.26, 148.21, 137.77, 136.04, 130.53, 128.12, 127.01, 126.52, 124.66, 122.50, 121.41, 17.86. MASS spektr: m/z $C_{13}H_{12}N_2O$: 212,1.

**N-(3-metilfenil)-pikolinamid**: 0,615 gr (0,005 mol) pikoli kislota va 1,07 gr (0,01 mol) m-toluidindan 0,062 gr (0,005 mol) $H_3BO_3$ katalizator ishtirokida sintez qilindi. $R_f$=0,85, $^{1}$H NMR (600 MHz, $CCl_3D$) δ 10.00 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (151 MHz, $CCl_3D$) δ 162.03, 149.96, 148.03, 139.05, 137.74, 128.98, 126.48, 125.22, 122.44, 120.40, 116.87, 112.31, 21.61. MASS spektr: m/z $C_{13}H_{12}N_2O$: 212,1.

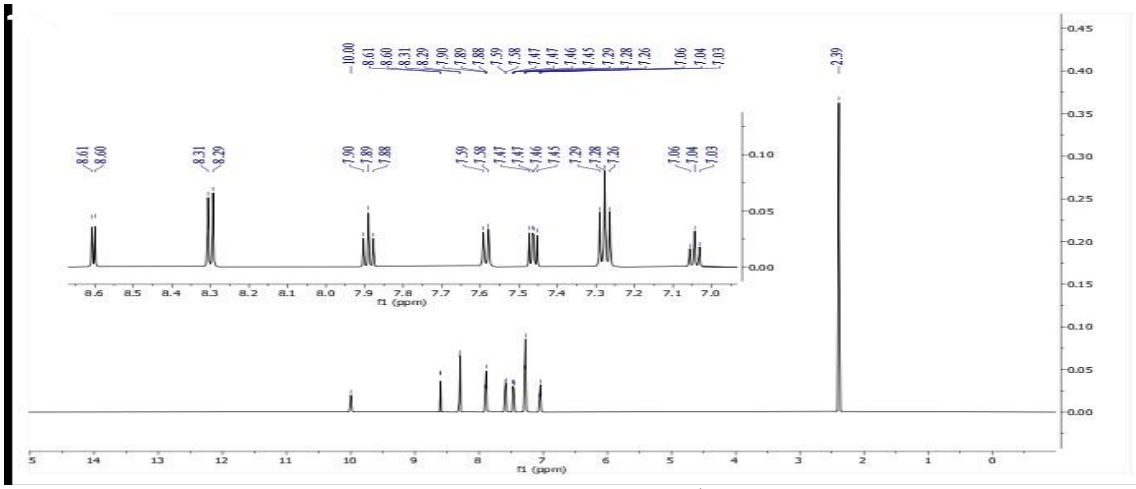
**N-(4-metilfenil)-pikolinamid:** 0,615 gr (0,005 mol) pikoli kislota va 1,07 gr (0,01 mol) p-toluidindan 0,062 gr (0,005 mol) $H_3BO_3$ katalizator ishtirokida sintez qilindi. $R_f$ = 0,82, suyqlanish harorati $T_s$=100°C. IQ spektr (KBr $sm^{-1}$) ν=3340 (-NH), δ=1520 (-NH), ν=1675 (-CO-).$^{1}$H NMR (600 MHz, $CCl_3D$) δ 9.97 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 8.29 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 3H). $^{13}$C YaMR (151 MHz, $CCl_3D$) δ 161.97, 150.07, 148.05, 137.76, 135.35, 134.03, 129.70, 126.46, 122.46, 119.69, 21.04. MASS spektr: m/z $C_{13}H_{12}N_2O$: 212,1



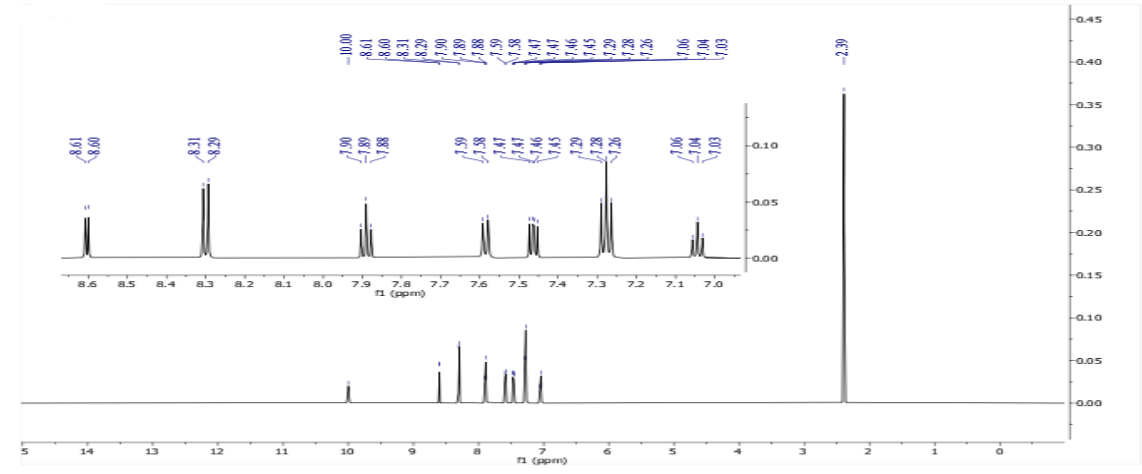
1-rasm: N-(2-metilfenil)-pikolinamidning IQ spektri



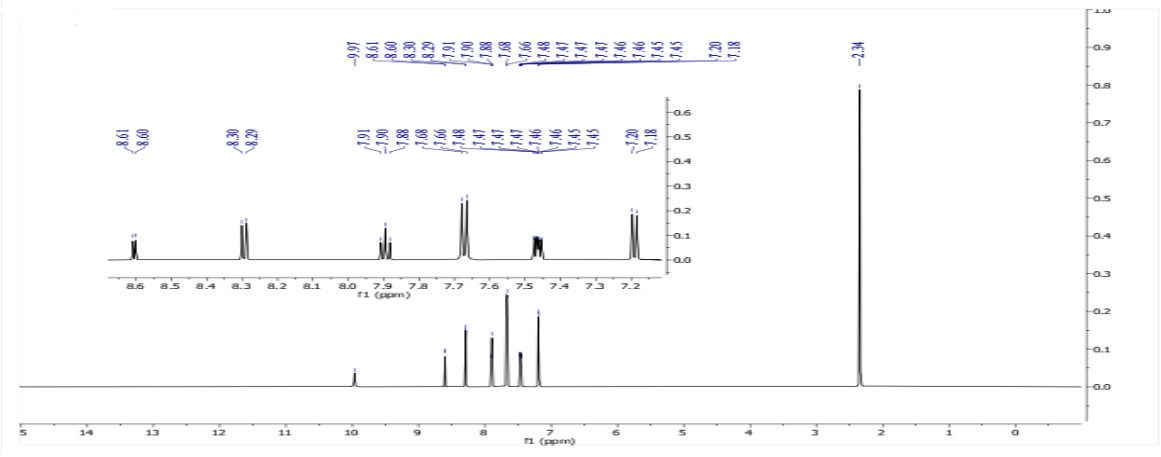
2-rasm: N-(4-metilfenil)-pikolinamidning IQ spektri



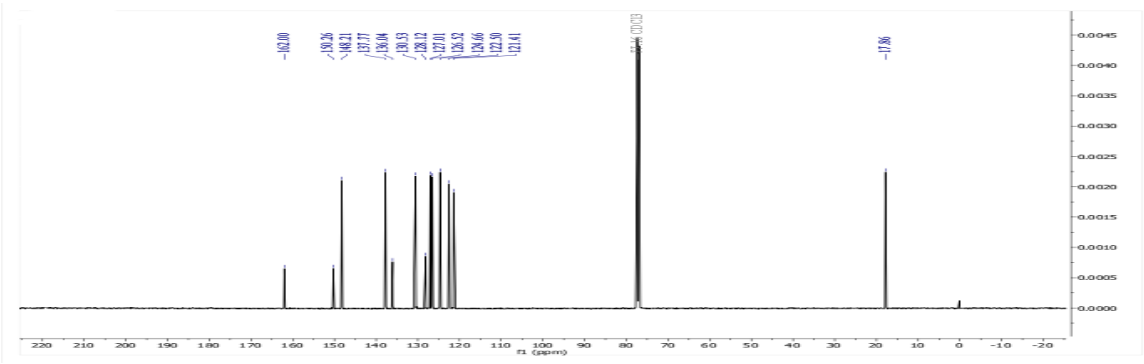
3-rasm: N-(2-metilfenil)-pikolinamidning $^{1}$H YaMR spektri



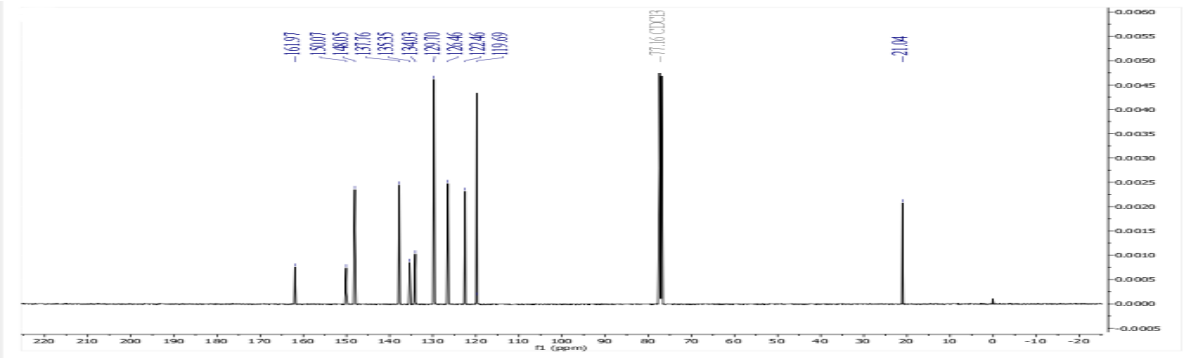
4-rasm: N-(3-metilfenil)-pikolinamidning 1H YaMR spektri



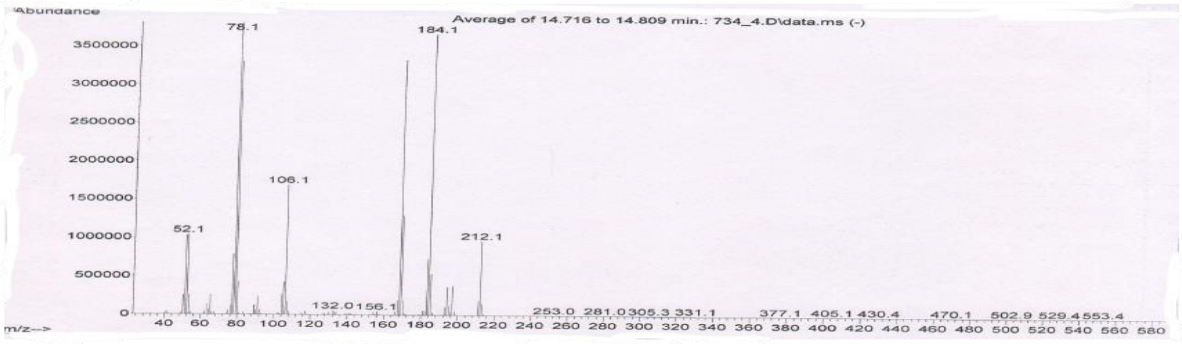
5-rasm: N-(4-metilfenil)-pikolinamidning 1H YaMR spektri



6-rasm: N-(2-metilfenil)-pikolinamidning $^{13}C$ YaMR spektri



7-rasm: N-(4-metilfenil)-pikolinamidning $^{13}C$ YaMR spektri




8-rasm: N-(2-metilfenil)-pikolinamidning MASS spektri

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